U.S. DEPARTMENT OF COMMERCE
National Technical Information Service

PB-252 818-T

THE IFP METHOD FOR SCRUBBING FUMES FROM A CLAUS UNIT

ENVIRONMENTAL PROTECTION AGENCY

1971

141034

PB 252 818-T

TR 377-73

Ph. Renault

THE IFP METHOD FOR SCRUBBING FUMES FROM A CLAUS UNIT

[Procédé IFP d'épuration des fumées d'unité Claus]

Pétrole Informations, 19 November 1971, pp. 27-33

Translated for the
ENVIRONMENTAL PROTECTION AGENCY
by
Translation Consultants, Ltd., Arlington, Virginia

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

BIBLIOGRAPHIC DATA SHEET	1. Report No. EPA TR73-377	2.	3. Recipient's Accession No. PB-252 818-T
4. Title and Subtitle IFP Method for Scrubbingfumes from a Claus Unit			5. Report Date 1971 6.
7. Author(s) Ph. Renault			8. Performing Organization Rept. No.
9. Performing Organization Name and Address Translated from the French by EPA			10. Project/Task/Work Unit No. 11. Contract/Grant No.
12. Sponsoring Organization Name and Address EPA ISD Translation Services Section Library RTP, NC 27711			13. Type of Report & Period Covered 14.

15. Supplementary Notes

Petrole Informations, 19November1971, pp. 27-33

16. Abstracts

17. Key Words and Document Analysis. 17a. Descriptors

EPA ISD
Industrial emissions
Desulfurization
Air Pollution Industrial Waste

17b. Identifiers/Open-Ended Terms

Sulfur recovery
effluent gases
catalytic conversion

17c. COSATI Field/Group 13B 68-A

PRICES SUBJECT TO CHANGE

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages
Exclusive permission granted NTIS for storage and distribution of this material	UNCLASSIFIED	18
	20. Security Class (This Page) UNCLASSIFIED	22. Price $3.50-2.25

Ph. Renault*

THE IFP METHOD FOR SCRUBBING FUMES FROM A CLAUS UNIT

Pollution caused by sulfur compounds has reached such a level that the situation can no longer be disregarded. In 1970, wastes poured into the atmosphere (in the form of sulfur dioxide) amounted to 18 million tons of sulfur in the case of the United States and about 8 million tons for Western Europe. These figures can be compared with the annual worldwide production of sulfur which reached 40 million tons in that same year.

It is therefore advisable to undertake measures with the utmost speed which will lead to reduction in the magnitude of this pollution.

At the present time, production of sulfur by the Claus method amounts, on an annual basis, to about 9 million tons for the Free World. At the limit, this production can already be considered as the result of a struggle begun as early as the 1950's against sulfur pollution. Indeed, the Claus units are mainly located in refineries and natural gas processing plants. Their importance began to grow shortly after conclusion of the Second World War.

At this time, hydrodesulfurizing methods began to make their appearance in the refineries. These methods had the effect of increasing the H_2S content of factory gases. It became necessary to scrub them and subsequently to transform the recovered H_2S into sulfur. On the

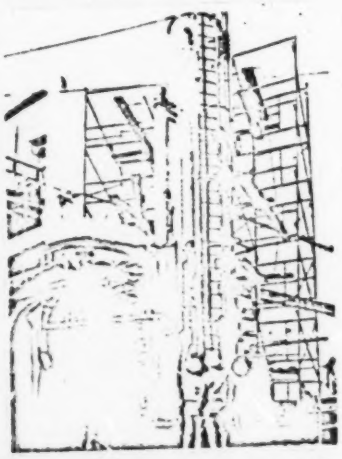
---

* Chief Engineer, IFP (Institut français du petrole - French Petroleum Institute)

other hand, the discovery at the beginning of the 1940's of a number of natural gas fields with a high H_2S content made necessary the separation of the H_2S before marketing. It was found difficult to burn it off in the effort to remove it. In this regard, a first Claus unit for transformation of H_2S into sulfur was built in the United States in 1944. There now exist in the world about 400 Claus units for production of sulfur, some of which with a capacity of more than 1000 tn/d such as those operated by the SNPA (Societe National des Petroles d'Aquitaine-National Firm for Aquitaine Petroleum) at Lacq and its subsidiary in Canada, Aquitaine of Canada which builds units with capacities close to 2000 tn/d.

Performance Data of the Claus Method

Flowcharting the Claus method shows two distinct steps, a first thermal step in which a third of the H_2S is burned into SO_2 followed by a second catalytic step in which the non-transformed H_2S reacts with the SO_2 to produce sulfur. In reality, the thermal step already produces a major conversion into sulfur whereby more than 50% of the potential sulfur can be formed there.



Reproduced from best available copy.

The semi-industrial sulfur recovery unit of Delta Projects at Lone Pine Creek in Alberta (Delta Projects doc.).

Figure 1 shows the thermodynamic equilibrium of the Claus reaction as a function of temperature:

$$2\,H_2S + SO_2 \rightleftarrows 3\,S + 2H_2O.$$

It can be seen that, in principle, it is advantageous in the catalytic stages to work at the lowest possible temperature. However, there are two situations preventing work being performed at the desirable level since:

the Claus reaction is exothermal (ΔH = -35 Kcal) and the temperature rises along the catalytic bed as the reaction moves forward;

too low a temperature leads to deposits of liquid sulfur on the catalyzer owing to its too low vapor tension.

In practice, a series of catalytic stages (2 to 3) is used, with between each one of them a stage for condensing the sulfur in such a way as to remove the vapor sulfur, thereby shifting the equilibrium in favor of conversion. The temperatures of catalytic converters are generally included between 220 and 320°C in the first stage and between 200 and 250°C in the following ones.

Figure 1 shows that under these conditions the conversion into sulfur is limited at each stage. The total recovery of a Claus unit is therefore on the order of 95 to 97% for a unit with three catalytic stages.

Figure 2 depicts the development of the yields and concentrations of acid gases in a Claus unit. Figure 3 shows that the addition of

supplementary stages will only slightly improve the sulfur production of the unit.

The effluent gases from a Claus unit are presently incinerated either catalytically or thermally so as to transform the sulfur compounds into SO_2. They are then passed out to the atmosphere through a stack. One response to the pollution problem used by the Claus units consists in building the stacks higher and higher in order to sufficiently disperse the SO_2. It appears probable that the long-term tendency will be to specify a maximum concentration at the stack inlet. There will also undoubtedly be a limited dilution at the incinerator. For this reason, the solution of building higher and higher stacks, furthermore a very expensive solution, will no longer be acceptable.

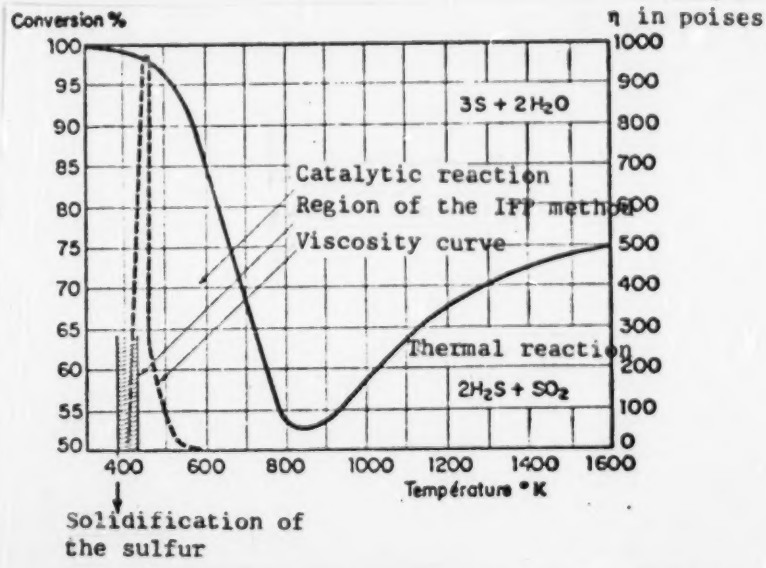


Fig.1. Thermodynamic equilibrium of the Claus reaction
$2H_2S + SO_2 \rightleftharpoons 3S + 2H_2O$

The IFP Scrubbing Process

The IFP has developed a method allowing reduction of the content of gases effluent from a Claus unit to a more acceptable level.

Principle of the Method

The basic reaction of the IFP method is the Claus reaction.

$$2H_2S + SO_2 \rightleftharpoons 3S + 2H_2O$$

It is carried on in liquid phase in a specific solvent in the presence of a dissolved catalyst. The solubility of the sulfur in the solvent is low and the sulfur produced is in this way continuously separated from the reactional environment shifting the equilibrium towards the right. According to Figure 1, low temperatures are favorable to high conversions. However, too low temperatures should be avoided since they introduce risks of clogging owing to the solidification of the sulfur ($\simeq$115°C). On the other hand, it is advisable to work at temperatures less than the viscosity maximum (180°C) of the sulfur (cf. Figure 2). Temperatures between 120 and 150°C are optimum.

The reactional environment developed by the IFP has the following advantages:

good catalytic stability;

good thermal stability of the solvent and catalyst;

low vapor tension of the solvent, amounting to 10^{-3} mm of mercury in operating conditions and, in this way, allowing losses owing to evaporation to be minimized;

the solvent allows an efficient liquid - gas contact without risk of frothing;

low solubility of the sulfur in the solvent;

the separation of the sulfur from the reactional environment is quite easy owing to the differing densities;

the solubility of the solvent in the sulfur is low, hence the quality of the sulfur produced is excellent;

the solvent and the catalyst are easily available commonplace chemical products.

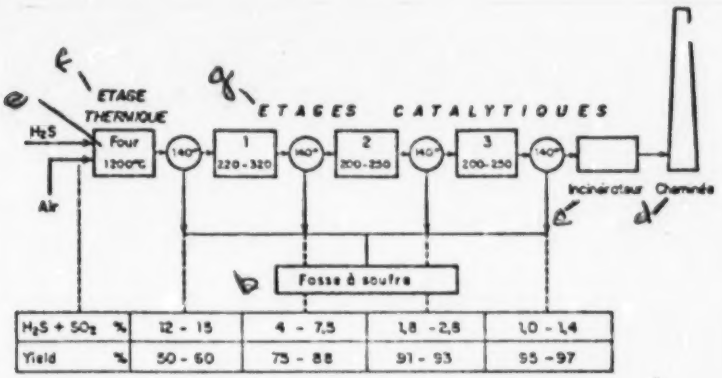
Operational Procedure for the Method

As shown in Figure 4, the IFP method has a very simple design and requires very little equipment.

The output gas from the Claus unit, generally available at a temperature on the order of 130-140°C and at a pressure slightly greater than atmospheric pressure, is processed as such by the IFP method. The reactor is a counterflow-filled column selected owing to the low loss of load exerted on the gas. The latter is fed into the bottom part of the reactor and comes out scrubbed through the top part. The liquid sulfur produced is separated by decanting and is continuously taken out through the bottom part of the reactor with monitoring of the interface. The solvent is returned at the head of reactor. The heat of reaction is removed by injection of the condensate into the recirculation loop. No degradation of the solvent is ascertained. The losses of solvent are quite low since they mostly

involve run-offs owing to the low vapor tension of the solvent (on the order of 10^{-3} mm of mercury). The catalyst is manufactured at the site using common products. It is fed continuously into the system by a metering pump. The heat exchanger shown on Figure 4 is used during the starting operation in order to raise the temperature of the solvent to a sufficient level.

Since the reactional environment is not corrosive, the unit is completely built from ordinary steel.



a. Fig 2 PROCEDE CLAUS CLASSIQUE

Legend: a. Figure 2. Standard Claus Method
b. Sulfur pit
c. Incinerator
d. Stack
e. Furnace
f. Thermal stage
g. Catalytic stages

As presently designed, the method is very easy to operate since:

it has a very great flexibility of operation with respect to variations in load both from the concentration as well as through-put viewpoint (operation at 30% base capacity is possible);

the loss of load is low and, since the transfers of mass from gas to liquid are reduced, the operative conditions along the

column are stable and well below the clogging limits.

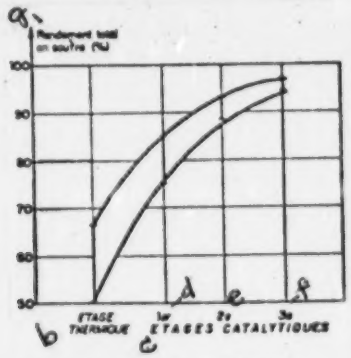


Fig 3. RENDEMENTS TYPIQUES D'UNITE CLAUS

Legend: a. Figure 3. Typical Yields of a Claus Unit
b. Thermal stage
c. Catalytic stages
d. 1st e. 2nd f. 3rd
g. Total sulfur yield (in %)

Furthermore, the method likewise operates as a means for removing the liquid sulfur often found in the gas to be scrubbed.

Field of Utilization of the Method and Operational Performance

Final concentration of the method.

The mean conversions with respect to the acid gases (SO_2 + H_2S) which can be obtained according to concentrations of the load are as follows:

H_2S + SO_2 % vol.	Conversion %
< 1	85
1 - 2	90
>2	95

H_2S/SO_2 ratio.

The H_2S/SO_2 ratio affects the conversion to the extent that it allows a theoretical maximum progress forward. It is desirable to

maintain this ratio between 2 and 2.5 so that the conversion is maximum. In practice, there are now continuously operating analyzers, using chromatography or UV spectrography, which are placed at the outlet of the Claus units. These analyzers report the H_2S/SO_2 ratio with a relative error less than 5% and allow automatic control of this same ratio at the outlet of the Claus units with a precision greater than 90%.

A good control of a Claus unit has another advantage. The conversion in the Claus unit improves as the H_2S/SO_2 ratio comes closer to 2. Therefore, the setting up of a chain of control of the unit is reflected by a slight increase in its sulfur production.

Effect of the COS and CS_2 Content

The thermal stage of the Claus unit leads to the formation of a quantity of COS and CS_2 owing to the presence in the charge of carbon dioxide (in concentrations varying according to the loads) and hydrocarbons (in low concentrations). Through a wise selection of operative variables, the first catalytic converter of the Claus unit reduces these contents to levels less than 1000-1500 ppm which is a concentration generally preserved in the later stages.

These constituents have no harmful effect on the IFP method and pass through it without undergoing a conversion. They therefore are still present in the outlet gas.

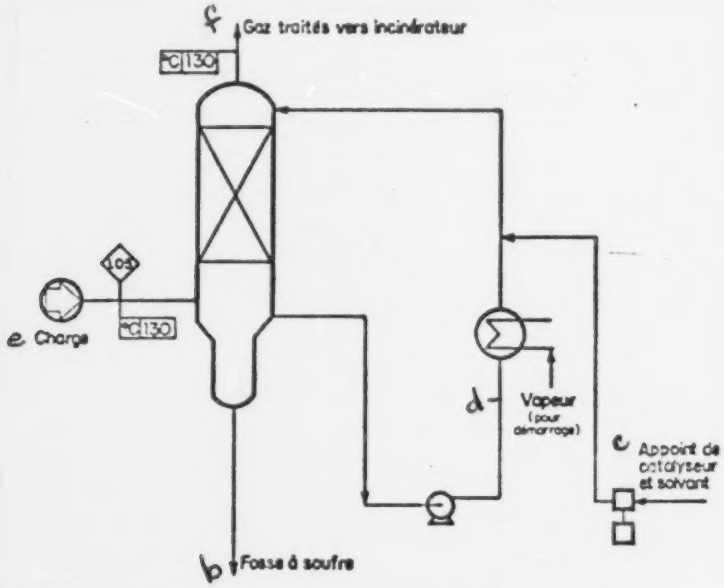
It is, for this reason, advantageous to produce concentrations of COS and CS_2 which are as low as possible at the inlet of the IFP process, hence at the outlet of the Claus unit. This can be done:

by increasing the temperature in the first converter;

by utilizing, instead of bauxite, more elaborate catalysts from the viewpoint of conversion of COS and CS_2 (activated alumina, cobalt-molybdenum based catalysts ...).

Typical Performances of the Method

These are shown in Table I. They correspond to the processing of residual gases by a same Claus unit, either after the second catalytic stage or after the third catalytic stage with the content of residual acid gases being identical in both cases. The production figures for sulfur are respectively 12 tn/d and 7.3 tn/d. The corresponding capacity of the Claus is 300 tn/d.



a Fig.4. PRINCIPE DU PROCEDE IFP D'EPURATION DE FUMEES D'UNITE CLAUS.

Legend: a. Figure 4. Principle of the IFP Process for Scrubbing Fumes Using a Claus Unit.
b. Sulfur pit
c. Addition of catalyst and solvent
d. Steam (for starting)
e. Load
f. Processed gases to the incinerator

TABLE I

PERFORMANCE FIGURES FOR THE IFP METHOD ADAPTED TO THE CLAUS METHOD

a	UNITE CLAUS AVEC DEUX ETAGES CATALYTIQUES	b UNITE CLAUS AVEC TROIS ETAGES CATALYTIQUES
c Capacité Nm^3/h	24.100	24.100
d Composition de la charge		
H_2S %	0,80	0,44
SO_2	0,40	0,22
S	0,37	0,37
H_2O	37,24	37,67
N_2	57,81	57,92
H_2	1,53	1,53
CO	1,24	1,24
CO_2	0,61	0,61
	100,00	100,00
e Gaz épuré		
H_2S %	0,080	0,080
SO_2	0,040	0,040
f Production de Soufre		
g — Soufre de réaction (kg/h)	375	189
h Soufre libre (kg/h)	112	112
Total kg/h	487	301
i — T/an	3.891	2.409

Legend:
a. Claus unit with two catalytic stages
b. Claus unit with three catalytic stages
c. Capacity
d. Composition of the Charge
e. Scrubbed Gas
f. Production of Sulfur
g. Sulfur of reaction (kg/h)
h. Free sulfur (kg/h)
i. tn/yr

Developmental Research

Investigation on the IFP method began in 1966. Research on a laboratory scale began using both synthetic fumes as well as actual fumes. During the year 1967, one pilot unit with a maximum capacity of sulfur of 30 kg/d was set up in the Center for Industrial Research and Development of the IFP at Solaize. This unit has operated continuously since that time. It allowed study to be made of the relationships

between different parameters such as:

selection of the catalyst;

conversion;

initial concentration of the acid gases in the fumes;

capacity;

reactional volume.

Research likewise involved all those subjects required for design of the industrial unit, i.e.:

different types of filling (in connection with the manufacturers);

corrosion;

instrumentation.

Industrial Applications

Table II shows the economic data relating to the two material balance sheets given in Table I.

The IFP method has now given rise to industrial solutions (cf. Table III).

The method is available in Japan through the intermediary of the Mitsubishi Heavy Industries engineering firm.

It is offered on the American continent (United States and Canada) by 5 contractors:

Delta Engineering, Houston, Texas;

Fluor Corporation, Los Angeles, California;

Ford, Bacon and Davis Construction, Dallas, Texas;

Olsen Engineering, Houston, Texas;

Ralph M. Parsons, Los Angeles, California.

TABLE II

THE IFP METHOD - ECONOMIC DATA

	a UNITE CLAUS AVEC DEUX ETAGES CATALYTIQUES	b UNITE CLAUS AVEC TROIS ETAGES CATALYTIQUES
c Investissements F.F.	3.000.000	2.600.000
d Unité montée en limite d'unité de fabrication.		
e Base française, Septembre 1971.		
f Ce coût ne comprend pas :		
g - les frais d'engineering		
h - les redevances de procédé		
i - la préparation du site		
j - les charges initiales de catalyseurs et produits chimiques		
k Solvant et Catalyseur		
l - charge initiale F.F.	180.000	145.000
m - consommation annuelle F.F/an	110.000	95.000
n Consommation d'utilités		
o - vapeur pour démarrage T.	48	38
p - condensat BP Kg/h	340	180
q - électricité kwh/h	85	70

Legend:
a. Claus unit with two catalytic stages
b. Claus unit with three catalytic stages
c. Investments
d. Unit installed as a limit of manufacturing unit
e. French base, September 1971
f. This amount does not include
g. - the engineering costs
h. - royalties for the method
i. - preparation of the site
j. - the initial loads of catalysts and chemical products
k. Solvent and catalyst
l. - initial charge F.F.
m. - yearly consumption F.F./yr
n. Consumption of Utilities
o. - steam for starting Tn
p. - low-pressure condensate kg/h
q. - electricity kwh/h

TABLE III

METHOD FOR SCRUBBING RESIDUAL GASES USING THE CLAUS UNIT.

UNITS LICENSED BY THE IFP

a SOCIETE	b LIEU	c CAPACITE Nm^3/h	d ETAT ACTUEL
Nippon Petroleum Refining C°	Negishi-Japon	28.400	e en fonctionnement
Idemitsu	Hirœji-Japon	26.700	f en construction
Kyokuto Petroleum	Chiba-Japon	18.600	f en construction
Showa Oil	Kawasaki-Japon	5.700	f en construction
Delta Projects Ltd	long Pine Creek Alberta-Canada	720	e en fonctionnement

Legend:
a. Firm
b. Place
c. Capacity Nm^3/h
d. Present state
e. Operational
f. Under construction

The 720 Nm^3/h capacity unit is in reality a demonstration unit and is the property of Delta Projects, subsidiary of Delta Engineering. Its photo is shown in the attached figure.

As far as the rest of the world is concerned, the IFP method is available through any engineering firm specializing in the field of sulfur.

It should be emphasized that the IFP method can likewise be applied to the recovery of sulfur beginning from the first-run effluents from ammonium sulfide brine strippers, either as is or combined with residual gases from the Claus unit.

Conclusion

Assuming that the Claus unit has the benefit of an efficient management and that it is sought to make a maximum improvement in

the selectivity for sulfur, recoveries of sulfur of 99% can be foreseen for the system including a Claus unit followed by an IFP unit. The IFP method for processing the residual gases from Claus units therefore supplies an advantageous solution within the scope of the struggle against pollution by sulfur compounds and further decreases considerably the SO_2 content in the waste gases from these units. The IFP method likewise has the advantage of producing sulfur which can be marketed easily by the consumer together with sulfur from the Claus unit.

The IFP likewise has under development methods for recovering sulfur:

by direct processing of refinery gas containing hydrogen sulfide;

beginning from power station fumes.